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DETERMINATION OF LOW COPPER IN STEELS AND IRONS BY ATOMIC ABSORPTION

EDNA F. JACOBSON
MATERIALS TESTING DIVISION

August 1971

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
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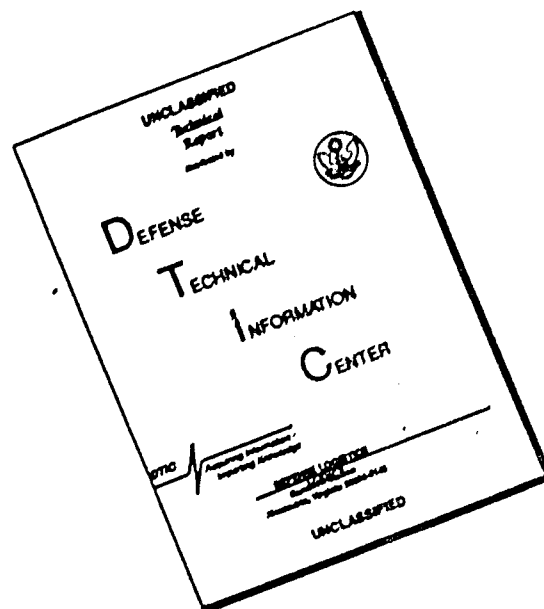
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DETERMINATION OF LOW COPPER IN STEELS AND IRONS BY ATOMIC ABSORPTION

Product Technical Report by

EDNA F. JACOBSON

August 1971

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An analytical method has been developed for the rapid determination of low copper (50 to 1800 parts per million) by atomic absorption. The method was successfully applied to different types of steels and irons, for example, low-alloy steel, stainless steel, tool steel, maraging steel, ingot iron, and cast iron. The detailed analytical method is appended to this technical report.

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I. INTRODUCTION

The determination of low copper in steels and irons is often required in quality assurance testing, research programs, and National Bureau of Standards cooperative certification. In electrogravimetric methods, large samples are required for low copper, many analytical separations have to be made, and the entire procedure is time-consuming. Photometric methods^{1,2} do exist which are very reliable; however, most photometric methods for low concentrations require organic solvent extractions and the need for high grade chemicals in order to eliminate the problems of high blanks. The cuprizone photometric method² eliminates the need of solvent extraction, but duplicate samples must be run in order to compensate for background color, and the presence of high nickel (15 percent and over) and cobalt (25 percent and over) interferes. Therefore, this method would not be applicable to maraging steels (20 percent nickel) and some of the newer experimental alloys.

Copper can also be determined spectrographically, and reliable results can be obtained. But, many more manipulations are required after sample dissolution than is required by atomic absorption analysis, thus making the spectroscopic determination of copper more time-consuming and costly.

Methods for the determination of copper in steel and cast irons by atomic absorption have been published^{3,4}. However, different instruments, burners, gas mixtures, and acid concentrations were used.

The atomic absorption method for copper developed under this study and appended to this report is very rapid. It is a direct method, that is, after dissolution of the sample in acid, the solution is diluted to volume, aspirated, and the copper content calculated. The only variation is in the presence of high silicon or tungsten, when a filtration after dissolution is required in order to avoid clogging of the aspirator.

Accurate results were obtained on 26 National Bureau of Standards samples including 16 steels, 1 maraging steel, 2 ingot irons, and 7 cast irons. In complex alloys, copper has been determined as easily as in a plain carbon steel.

¹ASTM Standards, Part 32, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores, ASTM Designation: E 30-70, Standard Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron, Copper by the Neocuproine Photometric Method, 1971, p. 71-73.

²MURRAY, W. K., *The Spectrophotometric Determination of Copper in Titanium and Other Metals with Dicyclohexanone Oxalyldihydrazone*, Army Materials and Mechanics Research Center, WAL TR 401/229, May 1958.

³BEYER, M., *The Determination of Manganese, Copper, Chromium, Nickel, and Magnesium in Cast Iron and Steel*, Atomic Absorption Newsletter, v. 4, no. 3, 1965, p. 212-223.

⁴KINSON, K., and BELCHER, C. B., *The Determination of Minor Amounts of Copper in Iron and Steel by Atomic Absorption Spectrophotometry*, Anal. Chim. Acta, v. 31, 1964, p. 180-183.

II. EXPERIMENTAL

In order to determine the effect of the acid medium on sensitivity, three standard copper solutions were prepared, each containing the same amount of copper. The three different media were dilute nitric acid, dilute perchloric acid, and dilute hydrochloric-nitric acid mixture.

Setting the wavelength at 3247 Å, which is the most sensitive line for copper, the instrument was set at zero absorbance by aspirating water. The three copper standard solutions were aspirated and absorbance recorded. The dilute hydrochloric-nitric acid mixture improved the absorbance over the dilute nitric acid alone, while the dilute perchloric acid gave practically no absorbance reading. The combination of hydrochloric and nitric acids is most desirable as it permits the easy dissolution of many iron-base materials.

The next step was to establish the optimum instrumental parameters with the atomic absorption instrument used at AMMRC, that is, Jarrel-Ash 82-546. The parameters shown in Table I were established:

TABLE I. INSTRUMENTAL PARAMETERS FOR THE JARRELL-ASH INSTRUMENT

Total Consumption	
Burner Height	Scale Number 0
Fuel	Hydrogen
Pressure	24 psi
flow rate	85 scfh
Support Gas	Air
Pressure	30 psi
Flow Rate	25 scfh
Wavelength	3247 Å
Current	4 mA-Normal
Voltage	610
Damping	Full

A set of standard solutions containing from 0.2 to 5.0 µg of copper per milliliter was prepared and aspirated. A straight line following Beer's law was obtained (see Figure 1).

To study the effect of iron on the copper calibration curve, several lots of pure iron were tested. As much as 37 to 933 parts per million (ppm) of copper were found in the pure iron samples. Such material would seriously limit both the upper and lower parts of a calibration curve.

A zone-refined iron was obtained and tested, and its copper content was found to be about 10 ppm. This level of copper could be conveniently tolerated. Figure 2 shows the effect of 1.0 and 0.50 g of iron on a typical calibration curve. The increased sensitivity of the 0.50 g of iron dictated the use of this amount in subsequent testing of National Bureau of Standards standard samples.

Over a range in which Beer's law applies, a linear relationship exists between the concentration and absorbance values. Accordingly, the slope of such a relationship can be used as a factor for converting absorbance values to concentration values and thus avoid the need for using calibration curves. Table II shows the factors obtained for one set of standard solutions which were added to the equivalent of 0.50-g samples of iron.

The averages of the factors obtained on other days were 10.26, 10.47, and 10.55. These can be considered to be in good agreement, but the slight differences indicate that a set of standards must be run from day to day in order to get the maximum reliability in analyzing unknowns.

Figure 1. Calibration curve —
copper in hydrochloric and nitric acids

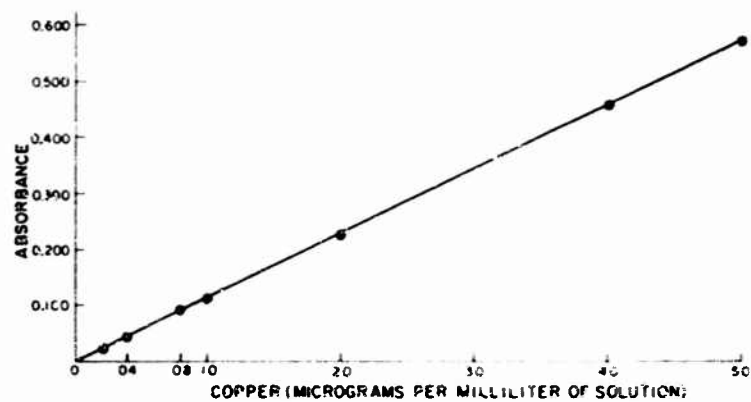


TABLE II. CONFORMANCE TO BEER'S LAW

Copper µg/ml	Corrected Absorbance	Factor = $\frac{\mu\text{g Cu/ml}}{\text{Absorbance}}$
0.25	0.025	10.00
0.50	0.048	10.42
1.50	0.147	10.20
2.50	0.238	10.50
5.00	0.477	10.48
7.00	0.649	10.79
9.00	0.846	10.64
Average		10.43

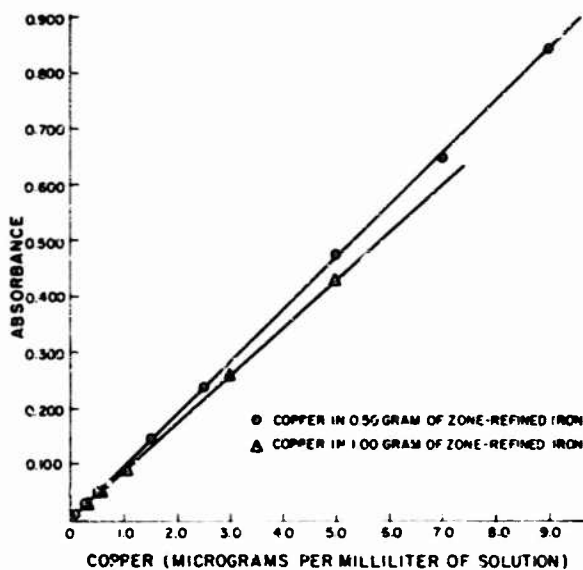


Figure 2. Calibration curve

III. TESTING OF NBS STANDARDS

In order to obtain information on accuracy and applicability to many types of ferrous materials, various NBS standard steels and irons were analyzed as unknowns. Because of the variety of materials tested, it would not be necessary to make a study of interfering elements, unless one particular type of material would produce results which were not comparable with the NBS certified values. Composition of the steels and irons used are shown in Tables III and IV, respectively.

TABLE 11. COMPOSITION OF NBS STANDARD STEELS

[illegible]

TABLE IV. COMPOSITION OF NBS STANDARD IRONS

Year	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	2438	2439	2440	2441	2442	2443	2444	2445	2446	2447	2448	2449	2450	2451	2452	2453	2454	2455	2456	2457	2458	2459	2460	2461	2462	2463	2464	2465	2466	2467	2468	2469	2470	2471	2472	2473	2474	2475	2476	2477	2478	2479	2480	2481	2482	2483	2484	2485	2486	2487	2488	2489	2490	2491	2492	2493	2494	2495	2496	2497	2498	2499	2500	2501	2502	2503	2504	2505	2506	2507	2508	2509	2510	2511	2512	2513	2514	2515	2516	2517	2518	2519	2520	2521	2522	2523	2524	2525	2526	2527	2528	2529	2530	2531	2532	2533	2534	2535	2536	2537	2538	2539	2540	2541	2542	2543	2544	2545	2546	2547	2548	2549	2550	2551	2552	2553	2554	2555	2556	2557	2558	2559	2560	2561	2562	2563	2564	2565	2566	2567	2568	2569	2570	2571	2572	2573	2574	2575	2576	2577	2578	2579	2580	2581	2582	2583	2584	2585	2586	2587	2588	2589	2590	2591	2592	2593	2594	2595	2596	2597	2598	2599	2600	2601	2602	2603	2604	2605	2606	2607	2608	2609	2610	2611	2612	2613	2614	2615	2616	2617	2618	2619	2620	2621	2622	2623	2624	2625	2626	2627	2628	2629	2630	2631	2632	2633	2634	2635	2636	2637	2638	2639	2640	2641	2642	2643	2644	2645	2646	2647	2648	2649	2650	2651	2652	2653	2654	2655	2656	2657	2658	2659	2660	2661	2662	2663	2664	2665	2666	2667	2668	2669	2670	2671	2672	2673	2674	2675	2676	2677	2678	2679	2680	2681	2682	2683	2684	2685	2686	2687	2688	2689	2690	2691	2692	2693	2694	2695	2696	2697	2698	2699	2700	2701	2702	2703	2704	2705	2706	2707	2708	2709	2710	2711	2712	2713	2714	2715	2716	2717	2718	2719	2720	2721	2722	2723	2724	2725	2726	2727	2728	2729	2730	2731	2732	2733	2734	2735	2736	2737	2738	2739	2740	2741	2742	2743	2744	2745	2746	2747	2748	2749	2750	2751	2752	2753	2754	2755	2756	2757	2758	2759	2760	2761	2762	2763	2764	2765	2766	2767	2768	2769	2770	2771	2772	2773	2774	2775	2776	2777	2778	2779	2780	2781	2782	2783	2784	2785	2786	2787	2788	2789	2790	2791	2792	2793	2794	2795	2796	2797	2798	2799	2800	2801	2802	2803	2804	2805	2806	2807	2808	2809	2810	2811	2812	2813	2814	2815	2816	2817	2818	2819	2820	2821	2822	2823	2824	2825	2826	2827	2828	2829	2830	2831	2832	2833	2834	2835	2836	2837	2838	2839	2840	2841	2842	2843	2844	2845	2846	2847	2848	2849	2850	2851	2852	2853	2854	2855	2856	2857	2858	2859	2860	2861	2862	2863	2864	2865	2866	2867	2868	2869	2870	2871	2872	2873	2874	2875	2876	2877	2878	2879	2880	2881	2882	2883	2884	2885	2886	2887	2888	2889	2890	2891	2892	2893	2894	2895	2896	2897	2898	2899	2900	2901	2902	2903	2904	2905	2906	2907	2908	2909	2910	2911	2912	2913	2914	2915	2916	2917	2918	2919	2920	2921	2922	2923	2924	2925	2926	2927	2928	2929	2930	2931	2932	2933	2934	2935	2936	2937	2938	2939	2940	2941	2942	2943	2944	2945	2946	2947	2948	2949	2950	2951	2952	2953	2954	2955	2956	2957	2958	2959	2960	2961	2962	2963	2964	2965	2966	2967	2968	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Preliminary tests were performed on two sets of cast iron samples, in order to determine which method of dissolution and filtering would be preferred. These samples must be filtered due to the high silica present, otherwise, clogging of the aspirator by the silica would occur. One set of cast irons was dissolved directly in the 100-ml volumetric flasks, diluted to volume, and then dry-filtered into another vessel. The second set of irons was dissolved in beakers, filtered into volumetric flasks, and then diluted to volume. Both sets of solutions were aspirated, and the results obtained (see Table V) indicated that either method was satisfactory. However, due to the high silica content, it is preferable to dissolve the sample in a beaker and then filter into a volumetric flask.

TABLE V. RESULTS FOR CAST IRONS BY DIFFERENT TECHNIQUES OF FILTERING

Sample No.	Filtering Before Dilution	Filtering After Dilution
7d (range 0.037-0.048)	0.041%	0.038%
7f (range 0.021-0.023)	0.021%	0.022%

(If a flask is used for the dissolution, it must be washed with ammonium hydroxide to remove the silica which adheres to the walls of the flask.)

A trial run was made on NBS standard sample 132a, which contains 6.2 percent tungsten, in order to see if any copper would be occluded or lost during the filtration of the tungstic oxide. The certified value is given as 0.120 percent copper with a range from 0.112 to 0.125 percent. The copper value obtained for this sample was 0.123 percent, indicating that this method could be used in the presence of high tungsten content. However, the tungstic oxide must be removed by filtration prior to the aspirating of the sample to avoid clogging of the aspirator.

The results obtained on the NBS Standard Samples are shown in Table VI for steels and Table VII for cast irons.

Some of the samples show duplicate results which were obtained on different portions of the samples and the copper content determined at different times. The results obtained by atomic absorption are calculated in percent so that the comparison between the NBS certified values and those found can be compared more easily. The difference in percent between the certified and found values is based on the certified values. The range shown is the lowest and highest values obtained by the various cooperators who had participated in the NBS standard cooperative testing program.

In reviewing the values found with the NBS certified values, the agreement can be considered excellent. The differences between the copper found values and the certified average values did not exceed 0.006 percent, except for sample 6d which differed by 0.008 percent. However, the range between the high and low results is greater in 6d than in any other standard sample listed. In all cases, except for one run of standard sample 12b, the results fall within the cooperators' range, and that one is 0.001 percent less than the lowest certified value.

The wide variety of material covered by these standards and the fact that only iron and copper were used for the preparation of the standard curve indicate that there is no interference from the many elements represented in the various types of metals used.

TABLE VI. COMPARISON OF RESULTS WITH NBS STANDARD STEEL SAMPLES

Sample No.	Type	Copper Range	Certified Average Copper, %	Copper Found, %	Difference Copper, %
10g	Carbon Steel	0.006-0.010	0.008	0.008 0.008	0.000 0.000
22b	Carbon Steel	0.007-0.012	0.009	0.006 0.007	-0.003 -0.002
11d	Carbon Steel	0.000-0.014	0.010	0.011 0.012	+0.001 +0.002
111b	Ni-Mo Steel	0.025-0.032	0.028	0.025 0.026	-0.003 -0.002
160	Cr-Ni-Mo Steel	0.047-0.060	0.053	0.047	-0.006
101	Stainless	0.050-0.062	0.055	0.057	+0.002
14e	Carbon Steel	0.065-0.080	0.072	0.071 0.073	-0.001 +0.001
73c	Stainless	0.077-0.082	0.080	0.082	+0.002
30e	Cr-V Steel	0.091-0.100	0.094	0.092	-0.002
153	Co-Mo-W Steel	0.091-0.110	0.099	0.100	+0.001
36a	Cr-Mo Steel	0.100-0.122	0.114	0.112	-0.002
132a	Mo-W-Cr-V Steel	0.118-0.125	0.120	0.124	+0.004
32e	Ni-Cr Steel	0.123-0.134	0.127	0.129	+0.002
19f	Carbon Steel	0.149-0.156	0.151	0.153 0.149	+0.002 -0.002
106a	Cr-Mo-Al Steel	0.149-0.166	0.156	0.152	-0.004
101d	Stainless	0.18-0.191	0.184	0.190	+0.006
115b	Maraging	---	0.025*	0.023 0.023	-0.002 -0.002

*This is a spectrographic standard and the average result was obtained from a Provisional Certificate; therefore, no range was available. This sample was analyzed at AMRC by the Neocuproine Photometric Method¹ with values of 0.023, 0.024, and 0.022 percent copper found.

TABLE VII. COMPARISON OF RESULTS WITH NBS STANDARD IRON SAMPLES

Sample No.	Type	Copper Range	Certified Average Copper, %	Copper Found, %	Difference Copper, %
4e	Cast Iron	0.005-0.016	0.010	0.012	+0.002
7f	Cast Iron (High P)	0.021-0.023	0.021	0.021	0.000
55c	Ingot	---	0.040*	0.039	-0.001
				0.037	-0.003
7d	Cast Iron (High P)	0.037-0.048	0.042	0.042	0.000
122c	Cast Iron	0.049-0.051	0.050	0.051	+0.001
55c	Ingot	---	0.065†	0.065	0.000
				0.063	-0.002
82a	Ni-Cr Cast Iron	0.071-0.080	0.076	0.077	+0.001
107a	Ni-Cr-Mo Cast Iron	0.098-0.111	0.103	0.103	0.000
6d	Cast Iron	0.136-0.166	0.151	0.143	-0.008

*This average result was obtained from a Provisional Certificate; therefore, no range was available.

†The provisional certificate shows a value of 0.066 percent copper. The 0.065 present value is given as the certified value in the NBS Catalog of Standard Materials. The range is not known.

IV. DISCUSSION

The most accurate way to prepare a calibration curve (or factor) is by the procedure described earlier in the report; that is, by adding known amounts of copper standard solution to the base metal. However, the calibration curves prepared for atomic absorption analysis do not have the same repeatability as do curves prepared for spectrophotometric analysis. This is understandable, for small changes in instrumental parameters may cause significant variations in the repeatability of a calibration curve. Even slight clouding of the mirrors may go unnoticed and cause changes. Thus, to maintain the same conditions for the unknowns as are used for the standards, the unknowns must be run at the same time, or within a period of time in which no instrumental changes are made or required.

The suggested preparation of standard solutions is very practical when a large number of copper determinations are needed. However, if a copper value is occasionally requested, then the preparation of a complete set of standards can become costly. It would be more feasible to run NBS standards for the preparation of the calibration curve (or factor). Three standards, containing

concentrations of copper at the very low, low or middle, and upper levels should provide a good calibration curve (or factor). In order to evaluate the feasibility of this technique, three NBS standard samples No. 10g, 111b, and 106a (0.008, 0.028, and 0.156 percent copper, respectively) were carried through the procedure, with NBS standard sample No. 10f (0.032 percent copper, range 0.030 to 0.037) treated as an unknown.

These standards do not have to be of the same type of material as the unknown. The three standards selected because of their copper concentration were a carbon steel, a nickel-molybdenum steel, and a chromium-molybdenum-aluminum steel. The standard steel treated as the unknown was a carbon steel. The net absorbances of the three standards were plotted and the curve was satisfactory (see Figure 3). The values obtained on NBS sample No. 10f were 0.033 and 0.033 percent, a difference of +0.001 percent from the certified value. However, if only one standard sample had been run in order to determine the factor for calculating the unknown, the results for 10f would be as shown in Table VIII.

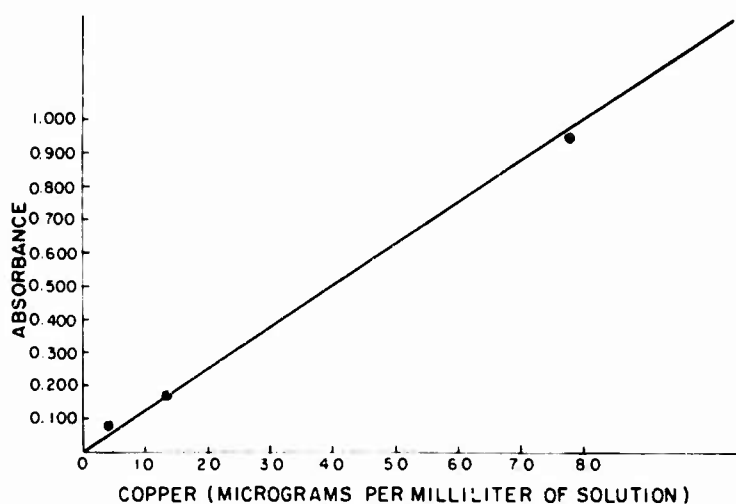


Figure 3. Calibration curve — using NBS standard samples

The results indicate that a slight bias can be obtained when calculating an unknown based on a single standard sample, particularly if the copper concentration is considerably above or below the amount present in the unknown.

One of the published methods³, though similar in the dissolution and preparation of the sample, used a Perkin-Elmer instrument and different conditions. One of the main differences was in the manner of standardization, wherein only one standard was used, and that

standard contained twice as much copper as the highest sample tested. Although a bias was evident, the deviations from the average certified values can be considered satisfactory for routine analysis.

As will be noted, the calibration curve obtained with the three NBS standard samples shows an increase in the slope in comparison with the previous calibration curve (Figure 2). This indicates that higher absorbance readings were obtained for the copper. This was not unexpected, since the mirrors were cleaned between the time of preparing the two calibration curves. This confirms how very important it is to obtain the calibration curve (or factor) under the same conditions as are used for the unknowns.

TABLE VIII. RESULTS FOR 10F BASED ON A FACTOR OBTAINED FROM A SINGLE STANDARD

Standard	Factor	Copper Found, %	Difference from Certified Value
10g	645.2	0.028	-0.004
111b	740.7	0.033	+0.001
160a	789.2	0.036	+0.004

In regard to spectrographic results vs atomic absorption results, the latter has produced reliable results with one more significant number, that is, ± 0.001 percent.

V. CONCLUSION

The atomic absorption method for copper in the range from 50 to 1800 ppm developed at AMMRC and described in the Appendix is capable of producing accurate and precise results. It can be applied with equal ease to all types of steel including plain carbon steels, alloy steels, maraging steels, tool steels, and ingot iron and cast iron.

Because of its accuracy, rapidity, and simplicity, the method can be used for both routine and certification analysis. In addition, for routine analysis the preparation of a calibration curve (or factor) can be simplified by running as few as three NBS standard samples along with the unknowns.

VI. RECOMMENDATION

It is recommended that this method be used in appropriate military specifications covering the determination of copper in low-alloy steels, stainless steels, tool steels, maraging steels, and ingot iron and cast iron. And it is further suggested that this method be submitted to ASTM for consideration as a standard method.

APPENDIX

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF COPPER IN STEELS, INGOT, AND CAST IRONS BY ATOMIC ABSORPTION

1. Scope

This method covers the determination of copper in concentrations from 50 to 1800 ppm.

2. Summary of Method

The sample is dissolved in hydrochloric and nitric acids. Any insoluble residue (silica or tungstic oxide) is filtered out, and the solution is diluted to a known volume. The solution is then aspirated using a total consumption burner with air and hydrogen as the oxidant and fuel, respectively. The micrograms of copper present in the sample is obtained from the calibration graph or by multiplying the absorbance by the factor obtained with the standard solutions.

3. Concentration Range

The recommended concentration range is from 0.1 to 0.9 μg of copper per milliliter of solution. This range may vary somewhat with different instruments.

4. Interferences

Interferences such as silica or tungstic oxide are removed by filtration in order to prevent clogging of the aspirator.

5. Apparatus

An atomic absorption spectrophotometer equipped with a copper hollow cathode tube and a total consumption burner that uses air and hydrogen.

6. Reagents

(a) Copper, Standard Solution A (1 ml = 100 μg Cu). Dissolve 0.1000 g of copper metal (purity: 99.9 percent minimum) in 10 ml of water and 15 drops of HNO_3 . When dissolution is complete add 10 ml of HCl . Transfer to a 1-liter volumetric flask, dilute to volume with water, and mix.

(b) Copper, Standard Solution B (1 ml = 1 μg Cu). Using a pipet, transfer 2 ml of copper solution A to a 200-ml volumetric flask, dilute to volume with water, and mix. Prepare fresh as needed.

(c) Iron Solution (1 ml = 0.050 g Fe). Dissolve 10 g of iron metal (copper, 10 ppm maximum) in 80 ml of HCl (1+1). When dissolution is complete, add HNO_3 dropwise until the iron is oxidized. Boil gently until oxides of nitrogen are expelled. Cool, transfer to a 200-ml volumetric flask, dilute to volume with water, and mix.

7. Preparation of Calibration Curves (or Factors)

(a) For Umpire Analysis

Using pipets, transfer 0, 10, 30, and 50 ml of copper solution B (1 ml = 1 μ g Cu) and 1, 3, 5, 7, and 9 ml of copper solution A (1 ml = 100 μ g Cu) to 100-ml volumetric flasks containing 10 ml of iron solution (1 ml = 0.050g Fe), dilute to volume with water, and mix.

(b) For Routine Analysis

(1) Transfer 0.500-g samples of NBS Standard Samples No. 10g, 73c, and 106a*, weighed to the nearest 0.5 mg, to 150-ml beakers.

(2) Add 5 ml of HCl (1+1) and heat gently until dissolution is complete†, oxidize with 10 drops of HNO_3 , and boil gently until oxides of nitrogen are expelled. Cool, add 10 ml of water, and bring to a boil. If silica or tungstic oxide is present, proceed to step (3); otherwise, transfer the solution to a 100-ml volumetric flask, dilute to volume with water, and mix.

(3) For solutions containing insoluble matter, add about 35 ml of water and bring the solution to a boil. If the insoluble matter is silica, filter through a 9-cm No. 41 paper; if it is tungstic oxide, filter through a double 9-cm No. 42 paper containing a small quantity of filter paper pulp. Collect the filtrate in a 100-ml volumetric flask. Wash the paper and residue about six times with hot water, cool, dilute to volume with water, and mix.

(4) Reagent Blank Solution. Carry a reagent blank through the entire procedure, using the same amounts of all reagents with the sample omitted.

(c) Photometry

(1) With the copper hollow cathode tube in position, energized and stabilized, locate the wavelength setting (in the vicinity of 3247 Å) that gives the maximum response of the detector system.

(2) Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero absorbance while aspirating water. Aspirate the standard copper solution, or the NBS standard sample solution, with the highest concentration. Adjust the burner, the air and fuel pressures and their flow rates, and the position of the capillary to obtain maximum response. A pressure of 30 psi for air and 24 psi for hydrogen, at respective flow rates of 25 scfh and 85 scfh, produced maximum response with the total consumption burner used to develop this procedure.

(3) Aspirate the highest copper solution a sufficient number of times to establish that the absorbance is not drifting. Record six readings and calculate the standard deviation, s , of the readings as follows:

*If the above standard samples are not available, select three standard samples that will yield about 0.5, 4.0, and 8.0 μ g Cu/ml when dissolved and diluted as described in 7 (b) (2).

†For certain types of material, 3 to 5 drops of HNO_3 added to the solution will aid in the dissolution. However, a large excess of HNO_3 is to be avoided. For some high-alloy steels, 15 drops of HNO_3 will be required for complete oxidation of the sample solution.

$$s = (A-B) \times 0.40$$

where

A = the highest of the six values found, and

B = the lowest of the six values found.

(4) For umpire analysis, beginning with the iron solution to which no copper was added, aspirate each calibration solution in turn and record its absorbance. If the value for the highest copper solution differs from the average of the six values by more than twice the standard deviation, s , as determined in step (3), above, or more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposits in the burner or clogged capillary), correct it, and repeat steps (2), (3), and (4).

(5) For routine analysis, use the same procedure as in step (4) but with the NBS standard sample solutions and the reagent blank solution.

(d) Calibration Curve (or Factor)

(1) For umpire analysis, subtract the absorbance found for the iron solution to which no copper was added from the value of each of the standard solutions.

(2) For routine analysis, subtract the absorbance found for the reagent blank solution from the value of each NBS standard sample solution.

(3) Plot the net absorbance values against micrograms of copper per milliliter or calculate the average factor as follows:

$$\text{Factor} = \frac{\text{micrograms of copper per milliliter}}{\text{net absorbance}}.$$

8. Procedure

(a) Test Solution. Transfer a 0.500-g sample, weighed to the nearest 0.5 mg, to a 150-ml beaker. Proceed as directed in 7(b)(2) and 7(b)(3).

(b) Reagent Blank Solution. Proceed as directed in 7(b)(4).

(c) Photometry. Check the instrument by aspirating the highest copper solution. If the absorbance value agrees with the value obtained previously, then proceed to aspirate the reagent blank and the test solutions, aspirating the highest copper solution after every fourth run. If the value of the copper solution does not agree with the previous value, the most likely sources of error will be deposits in the burner or clogged capillary tube. After cleaning the burner and capillary tube, rerun the copper solution. If the absorbance value agrees with the previous runs continue with the reagent blank and test solutions. If it does not agree, rerun the set of standard solutions and plot a new calibration curve (or calculate a new factor), and run the reagent blank and test solutions at the same time.

9. Calculation

Convert the net absorbance values of the test solution to micrograms of copper per milliliter by means of the calibration curve or the average factor. Calculate the ppm of copper as follows:

$$\text{Copper, ppm} = \frac{A}{B} \times 100$$

where

A = micrograms of copper per milliliter, and

B = grams of sample represented in the final volume.